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Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA

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Sludges generated at a wastewater treatment plant (WWTP) in Decatur, Alabama have been applied to agricultural fields for more than a decade. Waste-stream sources to this WWTP during this period included industries that work with fluorotelomer compounds, and sludges from this facility have been found to be elevated in perfluoroalkylates (PFAs). With this knowledge, the U.S. Environmental Protection Agency collected soil samples from sludge-applied fields as well as nearby "background" fields for PFA analysis. Samples from the sludge-applied fields had PFAs at much higher concentrations than in the background fields; generally the highest concentrations were perfluorodecanoic acid (≤990 ng/g), perfluorododecanoic acid (≤530 ng/g), perfluorooctanoic acid (≤320 ng/g), and perfluorooctane sulfonate (≤410 ng/g). Contrasts in PFA concentration between surface and deeper soil samples tended to be more pronounced in long-chain congeners than shorter chains, perhaps reflecting relatively lower environmental mobilities for longer chains. Several PFAs were correlated with secondary fluorotelomer alcohols (*sec*-FTOHs) suggesting that PFAs are being formed by degradation of *sec*-FTOHs. Calculated PFA disappearance half-lives for C6 through C11 alkylates ranged from about 1 to 3 years and increase with increasing chain-length, again perhaps reflecting lower mobility of the longer-chained compounds.

Introduction

For a little over a decade, a wastewater treatment plant (WWTP) in Decatur, AL has been permitted to apply sludge it generated on about 2000 ha of local agricultural land. Waste streams to this WWTP varied during this time, but are known to have included effluents from industries that conducted electrochemical fluorination and fluorotelomerization, as well as industries that worked with a variety of fluorotelomer compounds (FTCs) and perfluoroalkylates (PFAs). When sludges from this WWTP were analyzed for FTCs and PFAs they were found to be elevated relative to other sludges (see Supporting Information (SI); *1, 2)*. These elevated levels generated concern that the Decatur sludge applications might constitute an exposure route because application of sludges having high PFAs to soil has been documented to contaminate surface and drinking waters (*3*). Consequently, these elevated concentrations in the Decatur sludges spurred prudent efforts to decrease PFA loads to the WWTP, and sludge PFOA concentrations generated at the facility have fallen off dramatically since 2006 (Figure SI1). With this as background, in an effort to evaluate the impact of the sludges that had been applied to the Decatur fields, in late 2007 the U.S. Environmental Protection Agency (USEPA) collected and analyzed a small number of sludge and soil samples from fields that had received some of the highest sludge loads. These results documented the presence of high concentrations of several fluorotelomer alcohols (FTOHs) and PFAs in soils of the land-application areas.

The USEPA subsequently collected (November 2008) and analyzed water samples from a few Decatur, AL public drinking-water supplies. No levels of the perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS) were observed above the Provisional Health Advisories of 0.4 μg/L for PFOA and 0.2 μg/L for PFOS (*4*) in these municipal drinking-water samples. In February 2009, the USEPA collected additional water samples from selected private wells, agricultural ponds, and other surface waters located in and immediately around the land-application fields (*5*). Some of these samples were found to have PFA levels exceeding the Provisional Health Advisories.

An expanded set of surface and subsurface soil samples was collected in March 2009 to characterize the extent and magnitude of the PFA contamination in the land-application area. The general results of these efforts have garnered considerable attention in the lay press (*6, 7*), but the actual data have yet to be reported before now. In this paper, we report the analytical methodologies employed, the analytical results for both the 2007 and the 2009 surveys, and examine these data for patterns that illuminate the fate of these compounds. In a companion paper (*8*), we report analytical results for FTOHs, which have been shown to degrade to form some of the perfluorocarboxylates (PFCAs) we report here.

Materials and Methods

Sample Collection. Decatur, AL region soil samples were collected by USEPA regional scientists from (i) 2 sludge-applied fields and 1 sludge-free background field in September 2007; and (ii) 6 sludge-applied fields and 1 sludge-free background field in March 2009. One of the sludge-applied fields, 09H, received only one sludge application in the distant past. All sampled fields were in pasture; we plan to report upon analysis of grasses from these fields in a future paper. Table SI1 in the SI lists the sampled fields, documented sludge-application history, sample-identification numbers, and descriptions for the soil samples, and Figure 1 depicts the sampling locations.

The sampling equipment, composed of stainless steel, was washed three times with Optima-grade methanol (MeOH) prior to use. The samples were stored in certified-

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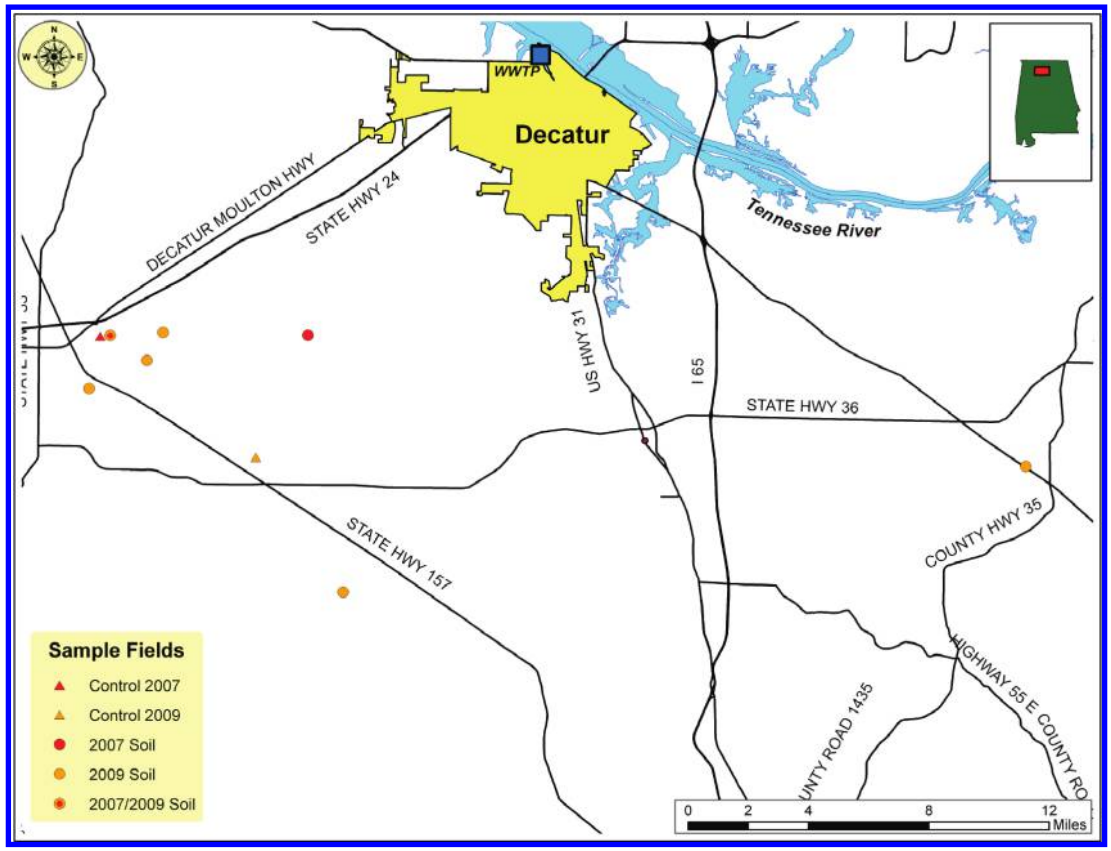

FIGURE 1. Sample locations for this study are south, and within an approximately 20-mile radius, of Decatur. Field numbers are not designated in the interest of preserving confidentiality regarding PFA concentrations of individual properties.

clean 500-mL, wide-mouth high-density polyethylene (HDPE) containers. The sampling equipment and containers were determined to be free of contamination for the intended analytes before the sampling trip by rinsing a representative of each item type with 60/40 (volume/volume) acetonitrile/water (ACN/H_2O) and analyzing the rinses. Surface-soil samples were collected from the 0- to 10-cm interval using sampling spoons, hand augers, and pans. Subsurface-soil samples were collected by Geo-probe from intervals bounded between the 23- to 56-cm and the 152- to 165-cm depths (Table SI1).

Quality-control samples taken to the field included Ottawa sand that has been shown to bear low concentrations of target analytes and a commercial top soil, the Cowart soil, for which the general range of concentrations of a variety of analytes has been documented to be low as well (*9, 10*). Also, duplicate field samples were collected from selected locations in the sludge-applied fields.

Chemicals. All chemicals used in this study were of the highest purity offered by the suppliers, uniformly ≥97% purity. We identify the chemicals we used in the Supporting Information.

Sample Preparation and Extractions. Field-moist samples from the 2007 sampling round were sieved through a MeOH-washed, 2-mm, stainless-steel sieve and extracted in triplicate. Because these samples yielded a high degree of variability in [FTOHs] between aliquots drawn from the same sieved sample (*9*), the 2009 sampling-round samples were homogenized by repeatedly passing them through 2-mm, stainless-steel sieves, coning and quartering until the sample was reduced to four approximately 1-g aliquots. Each of the four aliquots was transferred to a precleaned, labeled 16-mL polycarbonate (PPCO) centrifuge tube and sealed with a PPCO press-on cap; two of these aliquots were extracted for the PFA analyses reported herein and the remaining two were extracted for FTOH analyses which are reported in our accompanying paper (*8*). In addition, aliquots were removed from all samples to measure moisture content, by drying, which was used to calculate the concentrations reported herein on a dry-weight (dw) basis from the extractions which were performed on moist soils.

We extracted the 2007 and 2009 samples using different methods, but each was optimized for these sludge-applied soils as described below. For the 2007 samples, we performed an extraction designed to recover both PFAs and FTOHs from the same aliquot (*11*). We optimized this method for sludge-applied soils by extracting one sample seven times with MTBE to determine the number of steps necessary to balance satisfactory recoveries against diminishing returns with additional extraction steps. Based on this, we extracted the 2007 soils with four MTBE extractions in sequence, which we pooled for analysis, followed by an ACN extraction in accordance with the procedure described in our earlier paper (*11*). For the 2009 surface-soil samples we extracted the PFAs and FTOHs from separate aliquots drawn from each sample. For the PFAs, we used a modification of an ACN/H_2O extraction we reported upon earlier (*10*). Based upon exploratory efforts with a few sludge-applied samples from our 2007 survey, we deviated from our published ACN/H_2O extraction method for uncontaminated soils (*10*) by extracting these sludge-applied soils four times with 60/40 ACN/H_2O, which we pooled for analysis, but otherwise following our published method (*10*). Although we modified our extractions of these surface-soil samples as described above to accommodate their PFA-contaminated nature, we retained all other practices from our published methods (*10, 11*) including (i) spiking samples prior to extraction with $^{13}C_8$—PFOA as a recovery internal standard; (ii) subjecting extracts to ion-pairing cleanup to decrease analytical noise from natural organic matter that normally is concentrated in surface soils; (iii) reconstituting extracts in 60/40 ACN/H_2O with a suite of mass-labeled PFAs (Table SI3) present at 84 pg/g as matrix

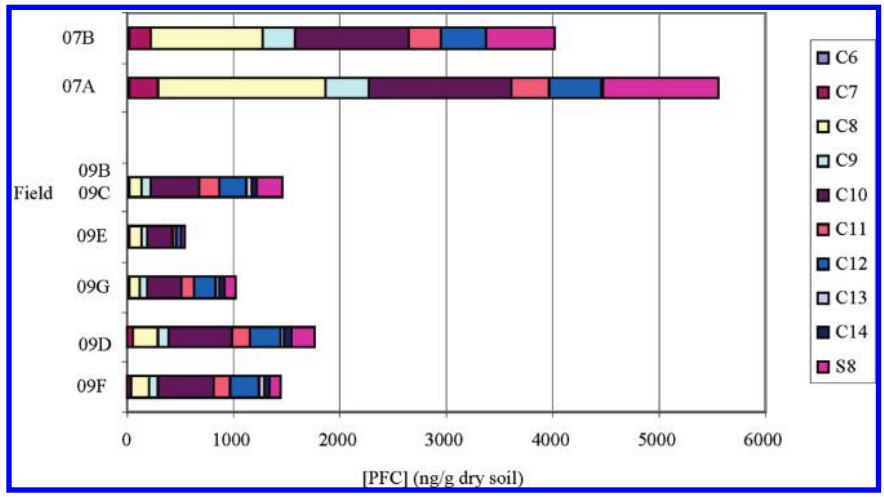

FIGURE 2. Geometric-mean surface-soil concentrations of analyzed PFAs within sampled fields. Results for the top two fields, 07A and 07B, are from the 2007 sampling campaign ($n = 4$ for 07B, $n = 3$ for 07A). The lower five fields are from the 2009 sampling campaign; fields 09B and 09C are contiguous and grouped together for this figure because they have similar sludge-application histories and only 3 samples between them ($n = 5$ for all other 09 fields).

internal standards; and (iv) running procedural blanks in which the extraction process was carried out on otherwise-empty extraction tubes. Additionally, we fortified selected samples from the 2009 campaign as a check of our analyte identification and quantitation.

Upon extraction of the 2009 samples, we discovered that all the subsurface soils exhibited poor returns of our mass-labeled recovery standard, $^{13}C_8$−PFOA, in contrast to satisfactory recoveries for all the surface soils. With exploration, we discovered that the relatively clay-rich subsurface samples tended to cohere into poorly permeable pellets when shaken on the Eberbach shaker table. When we performed the extraction again on the subsurface samples, replacing the shaker-table step with end-over-end rotation on a Labquake rotisserie, the subsurface soils did not pelletize and the $^{13}C_8$−PFOA recoveries fell in the satisfactory range as reported in the Results section. Because the subsurface soils were relatively low in natural organic matter, we found we could exclude the ion-pairing cleanup step on these samples with no deleterious effect.

Liquid Chromatograph, Tandem Mass-Spectrometer Analyses. Acetonitrile/water extracts were analyzed on a Waters Acquity ultraperformance liquid chromatograph (UPLC) interfaced with a Waters Quattro Premier XE tandem mass spectrometer operated in negative electrospray-ionization mode. Analytical methods are detailed in the Supporting Information along with an example of analytical results for an extract of a sludge-applied surface soil (Figure SI2).

Results

Data-Quality Metrics. In the Supporting Information, we report quality data reflecting on the field aspects of this study including (1) blanks and reference soil taken to the fields; (2) background-field samples; and (3) duplicate samples collected in the field. There were no anomalies among these metrics, except for the subsurface samples from the background fields (SI). These background subsurface samples returned detections for C6, C7, C8, and PFOS of about 4 orders of magnitude greater than their corresponding surface samples suggesting the possibility of low-level contamination of the subsurface sampling equipment for these analytes. For C6, C7, and C8, these detections still were an order of magnitude less than the detections in the sludge-applied fields, but PFOS was present in the background subsurface sample at about the same level as for the sludge-applied subsurface samples.

Quality data reflecting laboratory aspects of this study include (1) method blanks in which the extraction procedure was carried out in otherwise-empty tubes; (2) standard-curve back prediction; (3) recovery internal standards; and (4) standard additions to selected samples. All of these metrics indicate that the data in this study are of high quality (SI).

Results of Sampling in Sludge-Applied Fields. Analytical results for the samples from sludge-applied fields are tabulated in Tables SI9 for the 2007 survey and SI10 for the 2009 survey, and the average results for each field are depicted in Figure 2. For the 2007 survey, in fields 07A and 07B, the mass concentrations of analyzed PFAs sum to about 4−6 μg/g dry soil (Figure 2). In contrast, for the fields sampled in 2009, except for field 09H, mass concentrations of analyzed PFAs sum to only about 0.5−2 μg/g (Figure 2). Field 09H, which received only one sludge application in the distant past, had even lower PFAs, summing to <10 ng/g (Table SI10). Surface soils were sampled twice in each survey for one field, field B; while the number of samples is small, these data also show lower values in 2009 than 2007 (Figure SI3).

Considering all the data in whole, the dominant analyzed PFAs generally include PFDA (C10), PFOA (C8), and PFOS (S8), followed by PFDoA (C12), then PFUnA (C11), and PFNA (C9) (Figure 2). With the exception of PFOS, the analyzed perfluorosulfonates mostly were not detected. None of the unsaturated fluorotelomer acids were detected in either the 2007 or the 2009 survey. For the 2007 survey, the maximum analyzed concentrations (ng/g) of these dominant species were [C10] = 2100, [C8] = 2500, [S8] = 1400, [C12] = 1200, [C11] = 690, and [C9] = 650 (Table SI9). For the 2009 survey, however, the maximum analyzed concentrations (ng/g) of these dominant species were lower: [C10] = 140, [C8] = 320, [S8] = 410, [C12] = 530, [C11] = 310, and [C9] = 140 (Table SI10).

Discussion

These analytical results document that the majority of the Decatur soils in the sludge-application areas have concentrations of numerous PFAs well above background levels. Here we examine these data for patterns with respect to time, space, and precursors.

Sources of Variation in the Data: Sludge-Application Rate and Time Since Application. A simple visual-scan comparison of the 2007 and 2009 surface-soil data (Tables SI9 and SI10) reveals large general differences in PFA levels

TABLE 1. First-Order Disappearance Constants and Half-Lives Modeled from Surface-Soil Data

	PFA F statistics[a]		disappearance rate constant, half life			
	sludge app. rate	time since app.	supported[b]		unsupported[c]	
PFA homologue length (C no.)			k (yr^{-1})	$T_{1/2}$ (yr)	k (yr^{-1})	$T_{1/2}$ (yr)
6	**12.26**	**31.56**	1.04 ± 0.32	0.7		
7	**29.16**	**70.00**	0.81 ± 0.25	0.9		
8	**23.83**	**64.09**	0.71 ± 0.30	1.0	0.78	0.89
9	**21.72**	**26.96**	0.44 ± 0.25	1.6		
10	**19.86**	**14.76**	0.37 ± 0.14	1.9	0.53	1.31
11	**36.34**	*4.48*	0.25 ± 0.21	2.7		
12	**28.56**	2.57				
13	**48.01**	1.84				
14	**20.35**	1.17				
8 (PFOS)	**73.50**	**26.97**	0.57 ± 0.15	1.2		
Crit. F (0.05)	*4.26*	*4.21*				
Crit. F (0.01)	**7.82**	**7.68**				

[a] F statistics from analysis of variance to test whether variation among sample (n = 31) sludge application rates (7 application rates) or a linear-functional model through time (4 time increments) explains a significant component of variation relative to among samples sharing a common sludge-application rate or time since sludge application. Bolded F values are significant at p = 0.01 and italicized values are significant at p = 0.05. See text for details. [b] Supported values characterize disappearance rates of PFAs that likely are being generated by degradation of their precursors, e.g., sec-FTOHs. [c] Unsupported values are estimates of disappearance rates in the absence of being generated by precursors. See text for details.

between the two surveys, with analytes being generally higher in the 2007 survey than the 2009. There are numerous possible causes for these differences including variation of PFA concentrations between batches of sludge applied to the fields, variation in sludge-application rates between fields, elapsed time between sludge application to the fields and soil sampling, and variation of soil physical or chemical properties among fields.

Evaluation of the contribution of temporal variation in sludge [PFA]s to data set variance is limited because we have analyses of only a few Decatur sludge samples (Figure SI1); however, all the sampled fields received sludge during the years in which the anomalously high sludge [PFOA] values were recorded, specifically 2002 through 2006 (SI discussion, Figure SI1 and Table SI1).

The effect of "sludge-application rate" and "elapsed time between sludge application and soil sampling" on the data variance can be evaluated independently so long as these two variables are not correlated; Figure SI4 illustrates the absence of a statistically significant relationship between these variables, so the effect of each on soil [PFA]s can be evaluated. "Elapsed time between sludge application and soil sampling" might factor in data variance because increasing time offers the opportunity for numerous processes to act on the PFAs in the sludge-applied soils, potentially including: (1) uptake into plants; (2) erosive overland flow with precipitation events; (3) leaching through the soil column; (4) ingrowth from FTOH, and perhaps higher-order, precursors; and (5) degradation. If one or more of these processes controls a large part of the total variation in these data, then plots of PFA concentration vs time elapsed between sludge application and soil sampling might exhibit temporal trends. Homologous [PFCA]s are plotted in Figure SI5, and [PFOS] are plotted in Figure SI6, as a function of both "sludge-application rate" and "elapsed time between sludge application and soil sampling". Because these data are not bivariate-normally distributed, they cannot be statistically evaluated with simple correlation coefficients so we used an analysis of variance for unequal repeated measures (*12*). Table 1 presents a statistical summary of these plots. Figure SI5 and Table 1 reveal an interesting pattern wherein surface-soil [PFCA]s have a stronger statistical relationship (i.e., greater F statistic) with (1) sludge-application rate than elapsed time for the long-chain homologues; and (2) elapsed time between sludge application and soil sampling than for sludge-application rate for the short-chain homologues. Among possible causes for this pattern is that environmental mobility decreases and/or recalcitrance increases with increasing homologue length.

Given these data as well as those of our accompanying paper (*8*), we can inspect the data for evidence of whether leaching through the soil column and/or ingrowth from precursors might play a role in the temporal variability of the short-chain PFAs observed in these soils.

Depth Profiles. Soil samples were collected from up to three depths, i.e., the surface, ~50 cm, and ~150 cm, at each of three locations in two contiguous sludge-applied fields, 09B and 09C (Table SI10) and the background field, 09Bgd (Table SI6). Numerous PFAs were detected in the subsurface samples at all three sludge-applied sample locations (Table SI10), albeit, generally at lower concentrations in the deep soils than at the surface (Figure 3). When the concentration ratios of the mid-depth (~50 cm) to the surface and deep (~150 cm) to the surface are plotted as a function of chain length, a regular pattern emerges for all three sample locations wherein the subsurface/shallow ratios increase with decreasing chain length (Figure 4a and b). This pattern suggests that at least part of the reason that short-chains exhibit statistical decreases through time but long-chains do not (Table 1; Figure SI5) is preferential leaching of the short-chain congeners.

[PFCA] as a Function of [FTOH]. Wang et al. (*13*) has shown the 7:2 *sec*-fluorotelomer alcohol (7:2*s*FTOH; $CF_3(CF_2)_6CH(CH_3)OH$) to be a degradation product of the 8:2 primary fluorotelomer alcohol (8:2*n*FTOH; $CF_3(CF_2)_7$-CH_2CH_2OH) and proposed the degradation sequence of 8:2*n*FTOH → 8:2 fluorotelomer aldehyde → 8:2 fluorotelomer acid → 8:2 fluorotelomer unsaturated acid → 7:2*s*FTOH → PFOA. Following this logic, Ellington et al. (*9*), detected homologues of 7:2*s*FTOH, i.e., 9:2*s*, 11:2*s*, and 13:2*s*FTOHs, in a limited survey of Decatur sludge-amended soils. In our accompanying paper (*8*), we show a statistically significant functional dependence of the *s*-FTOHs on their *n*-FTOH precursors, suggesting that the longevity of the *s*-FTOHs is supported by degradation of their *n*-FTOH precursors. In Figure 5, we plot [PFCAs] as a function of both their *n*- and *s*-FTOHs. The PFCAs are significantly related to their *s*-FTOH precursors for PFOA, PFDA, and PFDoA, but not PFTeA. In

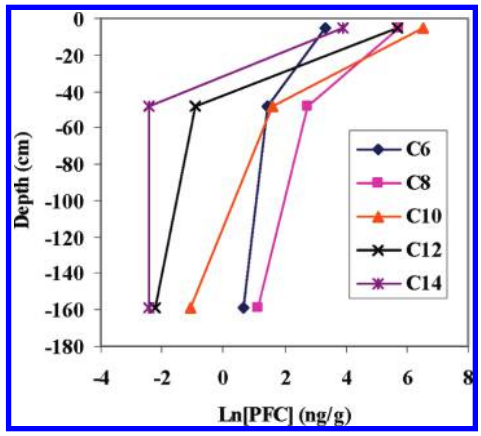

FIGURE 3. [PFA] (ng/g dry soil) vs depth for samples 09B3-1, 09B3-2, And 09B3-3. [PFA]s are transformed to the natural logarithms to facilitate depicting the wide concentration ranges among homologues and depths; nondetects are depicted at their limits of quantitation, also to ease depiction. With a few exceptions (Table SI10), analyte concentrations generally decrease or remain about the same with increasing depth. While only even-numbered PFCAs are depicted here, this relationship generally holds for odd-numbered PFCAs as well as PFOS (Table SI10).

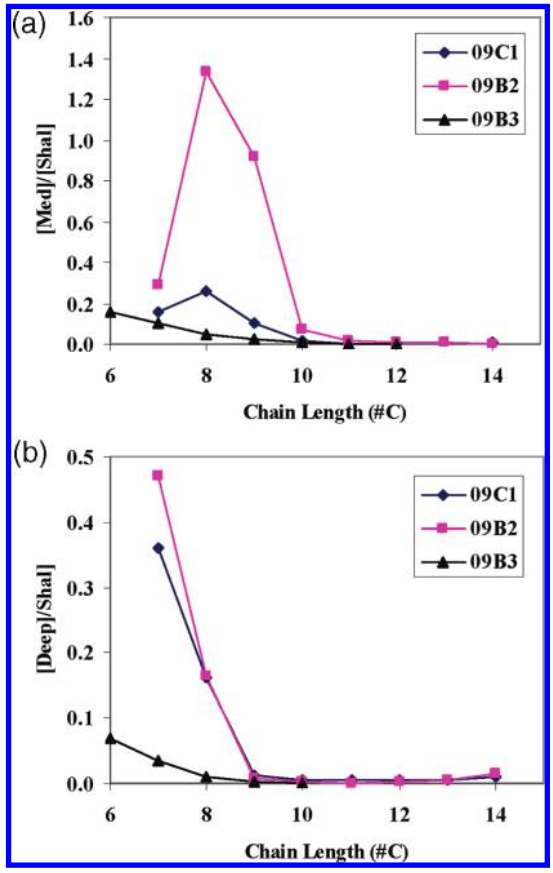

FIGURE 4. (a) [PFA] ratio (mid-depth/surface) at three sample locations. (b) [PFA] ratio (deep/shallow) at three sample locations. See text for discussion.

contrast, the PFCAs are correlated to their more remotely related *n*-FTOH precursors only for PFOA and PFTeA. The α oxidation of *n*-FTOHs to form odd-numbered PFCAs also has been identified as a minor biotransformation pathway (*14*); for this process, only 8:2*n*FTOH → PFNA exhibits a statistically significant relationship (Figure SI7). Taken as a group, these observations of significant relationships between some PFCAs and FTOHs supports the idea that part of their persistence in the sludge-applied soils is due to ingrowth from FTOH degradation.

Disappearance Half-Lives. Based on the observations presented above, at least part of the declines in short-chain [PFA]s through time (Figures SI5 and SI6) reflect a balance between losses from leaching (Figure 3), and perhaps other depletion processes, that are offset by ingrowth from *s*-FTOHs (Figure 5). While these processes commonly are modeled as first-order in the reactant (*15*), other more complicated factors might be at play as well. In the absence of evidence supporting such scenarios, however, we have modeled these losses as simple first-order. Nevertheless, it is important to realize that this modeling approach could significantly understate the persistence of these compounds in soil should more complex processes be active.

Supported Disappearance Half-Lives. The simplest first-order characterization of [PFA] loss through time reflects the effect of *support* by ingrowth from the chemical precursors, *s*-FTOHs, and the slope of linear regressions in ln[PFA]−time space yields estimates of supported first-order disappearance constants (k^s_{PFA}):

$$\ln[PFA] = \ln[PFA]_0 - k^s_{PFA}t \quad (1)$$

where $[PFA]_0$ equates to a statistical estimate of the PFA initial concentration when the sludge just has been applied. In turn, supported disappearance half-lives ($T^s_{1/2}$) for these compounds in the fields that have received applications of sludge containing these compounds can be calculated according to

$$T^s_{1/2} = \frac{\ln 0.5}{-k^s_{PFA}} \quad (2)$$

Supported first-order disappearance constants and half-lives of our analytes are tabulated in Table 1. These values of supported disappearance half-lives generally fall in the scale of years and increase with increasing chain length (Figure 6). This observation of half-life increasing with chain length is consistent with the observation that the ratio of subsurface- to surface-soil PFAs generally decreases with increasing chain length (Figure 4), possibly reflecting a stronger sorption affinity for soil of the long-chained homologues than the short-chains or a similar phenomenon.

The absence of unsaturated fluorotelomer acids in any sample (Tables SI9 and SI10) is noteworthy given their role as intermediates in the degradation of *n*-FTOHs to *sec*-FTOHs (*13*), both of which were in most sludge-applied surface-soil samples of our study (*8*). Assuming the unsaturated fluorotelomer acids are intermediates in the sludge-applied soils of this study, these nondetections suggest their disappearance half-lives are less than those we calculate for the perfluorocarboxylic acids (Table 1) or the FTOHs (*8*). Estimating the upper limit on half-lives of these acids using our detection limits (Table SI10), and eq 1 and the surface-soil 8:2*n*FTOH data of our accompanying paper (*8*), we estimate the disappearance half-life for the 8:2 unsaturated acid is <0.3 yr and the 10:2 unsaturated acid is <0.2 yr.

Estimated Unsupported Disappearance Half-Lives. Because supported PFA-fate properties evidently include the effect of ongoing ingrowth from degradation of *s*-FTOHs (Figure 5), these values (Table 1) likely overstate the persistence of these compounds when they are present in soil without any precursors. The persistence in soil of these compounds, in the absence of precursors, can be estimated according to the following (see SI for derivation):

$$[PFA] = \frac{k^u_{sFTOH}[sFTOH](1 - e^{-k^u_{PFA}t})}{k^u_{PFA}} + [PFA]_0 e^{-k^u_{PFA}t} \quad (3)$$

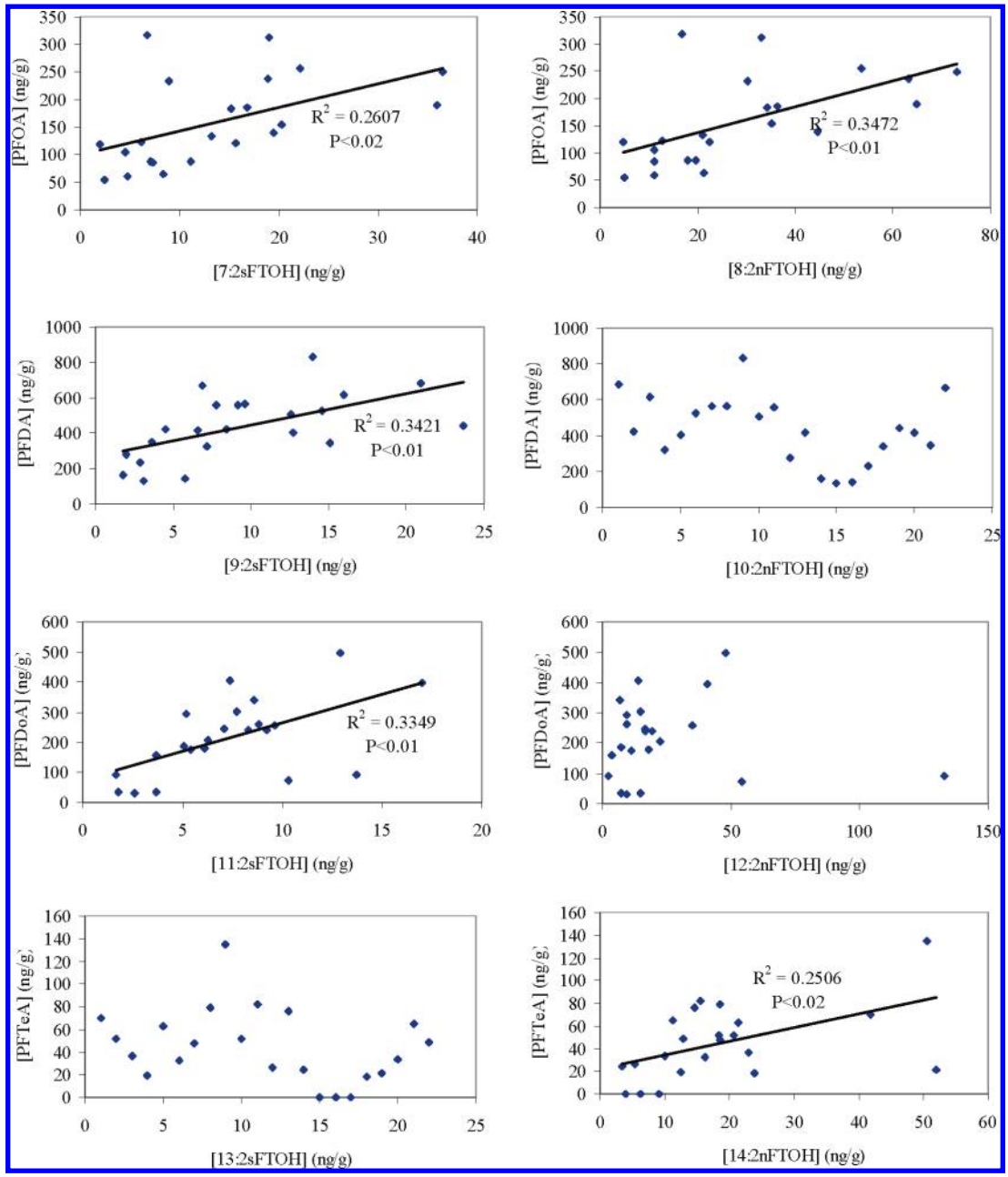

FIGURE 5. PFCAs in surface-soil samples ($n = 23$) as a function of FTOH precursors (ng/g dry soil). Acids generally are more strongly correlated with the *sec*-FTOHs than the *n*-FTOHs, presumably at least partly because the *s*-FTOHs are immediate precursors whereas the *n*-FTOHs are more remote precursors.

where k^u_{sFTOH} and k^u_{PFA} are the unsupported degradation constants of the PFA's precursor *sec*-FTOH and PFA, respectively. Equation 3 can be used to estimate the unsupported degradation constants of PFAs, given knowledge of the concentrations and unsupported degradation constant for the *s*-FTOH as reported in our accompanying paper (*8*), by taking the maximum [PFA] measured at 1.2 yr (Table SI1) to approximate $[PFA]_0$, and by minimizing the sums of squared errors between the estimated and observed values of [PFA]s as a function of k^u_{PFA} estimates. Estimates of unsupported degradation constants and half-lives are provided for PFOA and PFDA in Table 1. The estimated unsupported half-life for PFOA is 90% of the supported, and the unsupported half-life of PFDA is only 70% of its supported value.

Values derived from eq 3 are only as good as those of the input independent values. The values we used for unsup-

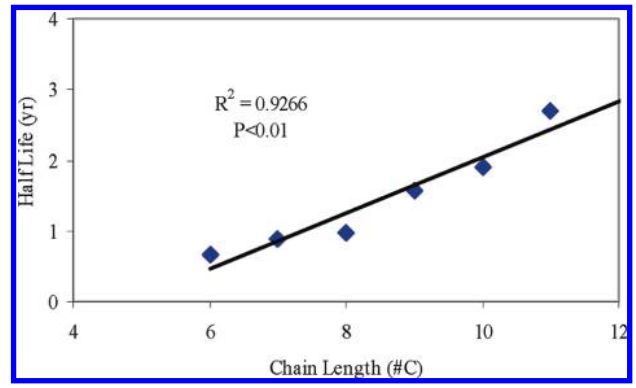

FIGURE 6. Calculated supported disappearance half-lives as a function of chain length ($n = 5$).

ported k^{u}_{sFTOH} were estimated from the concentrations of the *s*-FTOHs, their *n*-FTOH precursors, and calculated disappearance constants for the *n*-FTOHs (*8*). To the extent that the *n*-FTOHs were supported by precursor compounds, the resulting values for k^{u}_{sFTOH} and k^{u}_{PFA}, might be underestimated. In turn, the corresponding values for $T^{u}_{1/2}$ might be overestimates. We have no data on the presence or absence of *n*-FTOH precursor compounds, but polyfluoroalkylphosphoric acids (PAPs) (*16*) and fluorotelomer-based polymers (*11*) both are potential sludge constituents that have been shown to degrade to *n*-FTOHs. Considering all of this, our estimates of unsupported disappearance half-lives for PFAs in soils might best be considered upper-limiting values.

Perspective. In the sludge-applied surface soils we studied, PFA analytes summed to as high as ~5 μg/g and short-chain concentrations generally fell with increasing time since last sludge application. At least part of this decrease is from leaching losses to deeper soil. This loss evidently is offset by degradation of precursor compounds to form these analytes. Modeling the net losses of these PFA analytes from the surface soil as an analyte-first-order process, we get half-lives ranging from 1 to 3 years depending on chain length. These rough field-disappearance half-life estimates contribute to development of a useful perspective for environmental persistence of these compounds when cleanup and other options are being considered.

The relevance of the soil [PFA] data we report here to the general practice of application of sludge to land is unclear because much of the sludge that was applied to the fields in this study had substantially higher concentrations of PFOA, and likely other PFAs, than other sludges that have been reported in peer-reviewed literature (Figure SI1 and accompanying discussion).

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Supporting Information Available

This material is available free of charge via the Internet at http://pubs.acs.org.

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